ties ratio of the neighboring peaks of the oxidized and reduced forms corresponds to their content in the bombardment products of the sample. It is seen from Fig. 1, which depicts fragments of the BFA mass spectrum of the K₂[Co(CN)₅H₂O] complex, that with the elimination of the CN⁻ ligands, the stability of the lower degrees of oxidation of cobalt increases.

The results of the investigation carried out show that the use of the MS BFA method for studying the cyanides of transition metals makes it possible to obtain useful information on ligand elimination processes from the coordination sphere of complexes and on the redox reactions of these compounds.

LITERATURE CITED


NATURE OF THE INTERMEDIATE PRODUCT OF THE REACTION OF THE PENTACYANOCOBALTATE(II) ION WITH NITRIC OXIDE

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The reaction of the pentacyanocobaltate(II) ion with nitric oxide in aqueous solution was studied. Infrared spectroscopy and mass spectrometry with bombardment by fast atoms showed that the intermediate product formed in this reaction is a binuclear complex of cobalt containing bridge NO⁻ groups.

In recent years considerable attention of researchers has been attracted to the problem of activation of small molecules, such as those of nitrogen, hydrogen, oxygen, nitric oxide, carbon monoxide, etc. One of the possible pathways of activation of small molecules is complex formation with transition-metal compounds. The pentacyanocobaltate(II) ion [Co(CN)₅]⁻, which is an effective catalyst of numerous processes of hydrogenation of organic compounds by molecular hydrogen [1], is promising in this respect. Processes of complex formation of O₂, S0₂, and CO with the pentacyanocobaltate(II) ion have been described in the literature and can also be considered as pathways of activation of these small molecules [2-4]. It is known [5] that the end product of the reaction of the pentacyanocobaltate(II) ion with nitric oxide is the pentacyanonitrosyl complex [Co(CN)₅NO]⁻; however, no detailed study of this process had previously been conducted. The literature data show that the pentacyanonitrosyl complexes of cobalt may contain a coordinated NO⁻ anion or bridge hyponitrite groups N₂O₂ (in...
binuclear complexes) [6, 7]. Such coordinated NO groups can react with CO [6], which permits us to consider the complex formation of nitric oxide with [Co(CN)₅]³⁻ as a possible pathway of activation of NO in the course of the reaction with CO. The development of catalysts of the latter process is an urgent scientific and practical problem.

The subject of this work was a study of the reaction of the pentacyanocobaltate(II) ion with nitric oxide.

**EXPERIMENTAL**

Aqueous solutions of the pentacyanocobaltate(II) ion [Co(CN)₅]³⁻ were produced according to [5], and nitric oxide and carbon monoxide according to the procedure of [8]. The interaction of aqueous solutions of [Co(CN)₅]³⁻ with NO was studied spectrophotometrically in the absence of O₂. Oxygen was removed by several cycles of "freezing-evacuation" under vacuum. The reaction products were precipitated from solution by adding methanol. The kinetics of the decomposition of the intermediate product of the reaction of [Co(CN)₅]³⁻ with NO was studied spectrophotometrically in aqueous solution in the absence of O₂. Measurements of the optical density were performed at 19,800 cm⁻¹. The electronic absorption spectra in the region of 50,000-12,500 cm⁻¹ were recorded on a Specord UV-Vis spectrophotometer. The infrared spectra in the region of 4000-400 cm⁻¹ were recorded on a Specord 75-IR spectrometer in KBr tablets. To obtain mass spectra with bombarding by fast atoms we used a BBA ion source for the MX-1310 mass spectrometer with energy of bombarding argon atoms 3.5 keV [9]. Glycerin or triethylene glycol was used as the matrix for preparing the samples.

**RESULTS AND DISCUSSION**

An analysis of the changes in the electronic absorption spectrum of an aqueous solution of [Co(CN)₅]³⁻ during the interaction with NO in the absence of O₂ (Fig. 1) indicates the occurrence of two processes: the formation of an intermediate product characterized by an increase in the optical density in the region of 29,300 and 19,800 cm⁻¹; the formation of an intermediate decomposition product [Co(CN)₅NO]⁻, which was identified according to the known electronic and infrared spectra [5, 7]. We isolated the intermediate product formed in the first process in solid form and studied it by various physicochemical methods.

The positions of the absorption bands in the infrared spectrum of the intermediate product and their assignment are presented in Table 1. The characteristics of the IR spectrum of the end product of the reaction of [Co(CN)₅]³⁻ with nitric oxide, K₃[Co(CN)₅NO], which is dimerized to a substantial degree in solid form, are given for comparison. The data of IR spectroscopy show that the intermediate product isolated is a binuclear cobalt complex containing bridge nitrosyl groups. In the spectrum of the intermediate product bands are observed at 1050 and 980 cm⁻¹, which, analogously to the literature data [7], belong to the stretching vibrations of the N-O bond in the bridge hyponitrite group N₂O₂. We assigned the band at 1510 cm⁻¹, absent in the spectrum of K₃[Co(CN)₅NO], to the stretching vibrations of the N-O bond in the bridge nitrosyl-group of the intermediate product. The position of this band is evidence of coordination of the NO molecule in the form of the NO⁻ anion [6].

In the electronic spectrum of the intermediate product three absorption bands are observed at 43,200, 29,300, and 19,800 cm⁻¹; the last two are characterized by unusually high molar extinction coefficients for pentacyanide cobalt complexes (~10⁴ liters/mole·cm). Such spectra are characteristic of binuclear products of oxidative addition of many substrates to [Co(CN)₅]³⁻, including certain small molecules [2, 3], with the formation of a bridge between two cobalt atoms by the entering group.

We determined the composition of the intermediate product by BBA mass spectrometry; it is described by the formula [Co₂(CN)₁₀(NO)₃]¹⁺ (the spectrum contains signals of the ions \{K₅H₂[Co₂(CN)₁₀(NO)₃]⁺ at 665 amu and \{K₆H[Co₂(CN)₁₀(NO)₃]⁺ at 703 amu\). In the BFA mass spectrum of the complex signals of fragments containing ions formed in the decomposition of [Co₂(CN)₁₀(NO)₃]¹⁺ (A) are observed. Table 2 presents an identification of the lines observed in the BFA mass spectrum obtained. The singly charged positive ions presented are formed according to the usual valence rule [10]. Analogously to [Co₃(CN)₆X₃]²⁻, let us denote I (\{Co₃(CN)₆X₃\}³⁻). The formation of ions can be represented by the following general scheme of fragmentation: